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Patentanmeldung Nr. Patent application No. Demande de brevet n°

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Der Präsident des Europäischen Patentamts;
Im Auftrag

For the President of the European Patent Office

Le Président de l'Office européen des brevets
p.o.

R C van Dijk

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Organic acid resistance improvement in polymer coated metals

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Organic acid resistance improvement in polymer coated metals

Introduction

Polymer coated metals are developed for a number of applications. One of them is for manufacturing polymer coated metal containers for packaging organic acid containing stuff, such as tuna in white wine sauce.

The aggressiveness of organic acids such as acetic acid is different from that of other substances such as e.g. salt solutions, due to the different interacting mechanism. Whilst a salt-solution will primarily trigger corrosion processes, organic acid solutions are also capable of directly attacking the bond between the metal substrate and the polymer coating layer.

Without heat processing steps like pasteurisation and sterilisation, when packaging organic acid containing stuff, little or no delamination problems are found in spite of the organic acid being very aggressive and likely to attack the interface.

Known polymer coatings are specifically designed to show good adhesion of the coating after deformation.

However, according to the present invention, the problem of attack by organic acids like acetic acid is a more critical factor if the filled containers are heat processed, e.g. sterilised.

Problem definition

Organic acids are capable of diffusing through coatings in their non-dissociated state and the diffusion rate is strongly dependent on temperature (see table). At the polymer-metal interface, dissociation can take place and a.o. due to the accumulation of acid, the aggressiveness is high. The acid will have a double effect: it enhances corrosion and it detaches the coating.

Especially problematic in connection herewith is the effect of heat processing treatments (retort) used in the packaging of food to increase the storage life. These heat treatments vary with the content and take place at from 80 °C in hot fill applications to more than 120°C for periods that may well exceed 1 hour.

For example, many fish products packed in cans are sterilised at approx. 115 °C. This heat treatment

is an important factor in formulating a good product and process to package this type of products.

Presently for packaging such a product no polymer coated metal container is available. Therefore the research aim was to find a suitable solution for packaging acetic acid and other organic acid containing stuff that are heat processed, e.g. sterilised.

Prior art

US2003/0198537 provides a method to inhibit delamination of an extruded thermoplastic polymer coating from a container body by inductively heating the open end of a container body, prior to affixing the can end to the body, to adhere the polymer to the container. A container body is made by forming a cylindrical body having an exterior surface, an interior surface and an edge defining an orifice. The body interior surface is coated with a polymeric liner and the body exterior surface may optionally be decorated. The container body edge near the orifice is inductively heated and an end is joined to the body to form a completed container.

According to US2003/0198537 inductively heating the container body near the orifice inhibits delamination of extruded thermoplastic polymer coatings from container bodies as a result of container formation operations.

Present Invention

According to the present invention, heating the container body near the orifice is insufficient to prevent problems associated with packaging organic acid containing stuff that are heat processes, e.g. sterilised.

According to the present invention it is essential to heat the whole container to make sure that the whole polymer coating becomes resistant to the adverse effects of heat processing such as retorting in the presence of an organic acid such as acetic acid. In the context of this application the whole container means all parts making up the container that are made of polymer coated steel and that underwent substantial deformation, i.e. deformation to a degree that there is a risk of weakening of the interface between metal and polymer, e.g. the container body and/or the lid.

From the experiments it is clear that neither just any nor only a local heat treatment are sufficient.

In US2003/0198537, it is mentioned that the polymer needs to flow into the microsurface

imperfections in the can body interior surface. This already happens above the glass-point of the polymer when the polymer is in the amorphous phase.

According to the present invention however, only a heat treatment above the melting point of the polymer is sufficient to make the coating resistant to organic acid.

The specific use of induction heating to treat the container is not mandatory. It was found that the effect of the invention can also be achieved with a 'normal' oven treatment. This also results in the protection of the container. However, a heat treatment by induction (or any other fast heating method or "flash heating") is advantageous to forestall unwanted degradation and thus resulting embrittlement of the polyester chains in the presence of oxygen.

It was further found according to the invention that it is essential to observe certain time periods for the heat treatment to have optimum effect. From the examples, it is clear that longer periods of time are detrimental and a period of approx. 4 sec was optimal for the packagings under consideration.

Summarising, according to the present invention it is essential for a polymer coated metal container to be suitable as a heat processable, e.g. retortable packaging for organic acid containing stuff, to heat on the container's inside, the polymer to a temperature above the melt temperature of the polymer during a critical period which should be not too short to have effect and preferably not too long to forestall degradation of the polymer, for conventional polymer coated metal containers preferably in the order of less than 5 seconds.

Experimental work

Several factors are of influence on the resistance of polymer coated ECCS packaging steel to organic acids, viz. the type of polymer used because the chemical resistance to acids varies among polymers applied in polymer coated packaging steels, the chromium layer thickness since an increase in layer thickness increases the resistance, the coating thickness since increased coating thickness increases the barrier, the crystallinity of the polymer since increased crystallinity increases the diffusion barrier, additives in the polymer layer which may increase barrier properties and air entrapment since air pockets between coating and substrate are places where acids can accumulate and cause detachment of the polymer from the metal surface.

For flat, non-deformed materials, an optimum combination was found of chromium layer and polymer coating. During subsequent experiments with deformed materials, the positive effects of

material choice were lost to a large extent. It was shown that the attack of acetic acid during heat processing occurs at the places with the highest deformation rate, probably resulting from a weakened interface of the polymer and the steel.

Improving the adhesion of the starting material (flat plate) did not improve the performance of the product. It was therefore concluded that the only option to come to a full solution is to strengthen the interface after the making of the container and before filling and heat processing, e.g. retorting.

One option to achieve this is to heat the polymer in an air oven, to enable the binding groups of the polymer to direct themselves to the surface. Experiments were carried out with heating cans made from ECCS coated with PET (in this test deep drawn cans were used (DRD cans, Draw-Redraw)) at several temperatures (ranging from 90 to 260°C, i.e. ranging from slightly above the glass transition temperature to slightly above the melting point of PET) and for several periods (5 min. to 50 minutes) in a hot-air oven. Cans were exposed to 5 wt % acetic acid solutions and pasteurised for 1 hour at 100°C. These experiments showed that the only way to improve performance adequately was to completely melt the polymer to restore the functionality (see table).

A problem arising while restoring the functionality by heating the polymer above the melting point was the severe embrittlement of the polymer due to the relatively long residence times at these high temperatures. Even though the adhesion and corrosion resistance was restored, the coating became too brittle and no robust can was the end result. The solution to this problem was found in the use of fast heating methods, herein also referred to as flash heating. Here, inductive heating was used, but other methods are applicable as well. With these heating methods, it is possible to melt the polymer coating of a can within a few seconds.

It was shown that the heated DRD-cans were able to resist sterilisation cycles up to 90 minutes at 121°C with acetic acid concentrations up to 5 wt % (see table).

Analysis of the can wall and bottom showed that the coating itself was not changed to a large extent: crystallinity remained the same, orientation was only slightly lower for the DRD-cans. Subsequent crystallisation of the coating again gave a somewhat better result, although much lower than the effect of the melting step.

Experimental results

Diffusion through free film

The table shows the diffusion of acetic acid from a 3 wt % solution to demineralised water through a PET foil. This shows the importance of temperature on diffusion of acetic acid and organic acids in general on the diffusion coefficient. It also shows why heat treatments of acetic acid containing food are so aggressive to packaging steel.

Table: Diffusion of acetic acid through a PET foil (20 μm). (Volume cel: $4.40 \cdot 10^{-5} \text{ m}^3$; Membrane surface: $4.91 \cdot 10^{-4} \text{ m}^2$)

Temp.	[H3O+]	[HAc]	Tot.diffusion	D	S
(°C)	(mol/l)	(mol/l)	(mol)	(mol/m ²)	(mol/m ² s)
20	7.90E-08	3.94E-10	8.96E-09	1.83E-05	1.27E-08
60	2.40E-07	4.27E-09	9.70E-08	1.98E-04	1.37E-07
90	5.62E-05	1.81E-04	4.11E-03	8.38E+00	5.82E-03

Hot air oven heating of polymer

This table shows the effects of heat treatments in a standard hot air oven. It shows that the main improvement effect takes place above the melting temperature of the polymer.

Table: Performance of polymer-coated cans during 60 minutes exposure to 5 wt % acetic acid at 100°C, after heat treating the cans according to table.

5 min. 90°C	5 min. 125°C	5 min. 170°C	5 min. 220°C	5 min. 260°C
Poor	Poor	Slightly better	Slightly better	Good, no corrosion visible
10 min. 90°C	10 min. 125°C	10 min. 170°C	10 min. 220°C	10 min. 260°C
Poor	Poor	Slightly better	Slightly better	Good, no corrosion visible
25 min. 90°C	25 min. 125°C	25 min. 170°C	25 min. 220°C	25 min. 260°C
Poor	Poor	Slightly better	Slightly better	Good, no corrosion visible
50 min. 90°C	50 min. 125°C	50 min. 170°C	50 min. 220°C	50 min. 260°C
Poor	Poor	Slightly better	Slightly better	Good, no corrosion visible

As was mentioned above, although the results here seem acceptable, the embrittlement of the coating makes this method unusable, even at the shortest times used.

Inductive heating of polymer

DRD-cans were inductively heated to investigate the melting behaviour of the polymer coating. The table shows the different treatments and their success in melting the polymer.

Coating thickness (μm)	Inductor power (kW)	Heating time (s)	Visual result on polymer
20	10	4	Non-melted zone
20	10	5	Non-melted zone
20	10	6	Non-melted zone
20	10	10	Slight yellowing of coating (degradation)
20	20	2	Non-melted zone
20	20	3	Non-melted zone
20	20	4	Good, completely melted
20	20	5	Good, completely melted
20	20	6	Slight yellowing of coating (degradation)
20	20	10	Degradation of coating
20	40	2	Slight yellowing of coating (degradation)
20	40	3	Slight yellowing of coating (degradation)
30	20	4	Non-melted zone
30	20	5	Good, completely melted
30	40	2	Non-melted zone
30	40	3	Good, completely melted
30	40	4	Slight yellowing of coating (degradation)

All fully melted coatings were tested and showed a good resistance to acetic acid solutions, ranging up to 5 wt % acetic acid (tested 1 hour at 100°C) and 1.5 wt % (tested 90 minutes at 121°C). For unmelted cans, complete coating detachment occurred in this test and cans turned black due to corrosion product build-up.

Inductively heated cans exposed to acetic acid

In Fig. 1 two cans are shown that were exposed to 1.5 wt % acetic acid for 90 minutes at 121°C. The can without inductive heat treatment (left) shows delamination and corrosion over the whole surface as is mainly clear from the black colour. The can with inductive heat treatment (right) shows no corrosion or delamination.

Claims

1. A method to inhibit the attack by organic acid such as acetic acid, of a thermoplastic polymer coated on a metal container body and/or end, said method comprising flash heat treating the whole respective polymer coated metal parts of the container intended to come into contact with the organic acid such that the polymer on said parts is heated to above its melting temperature to make the container suitable for packaging organic acid containing stuff.
2. A method according to claim 1, wherein flash heat treating takes place by induction heating.

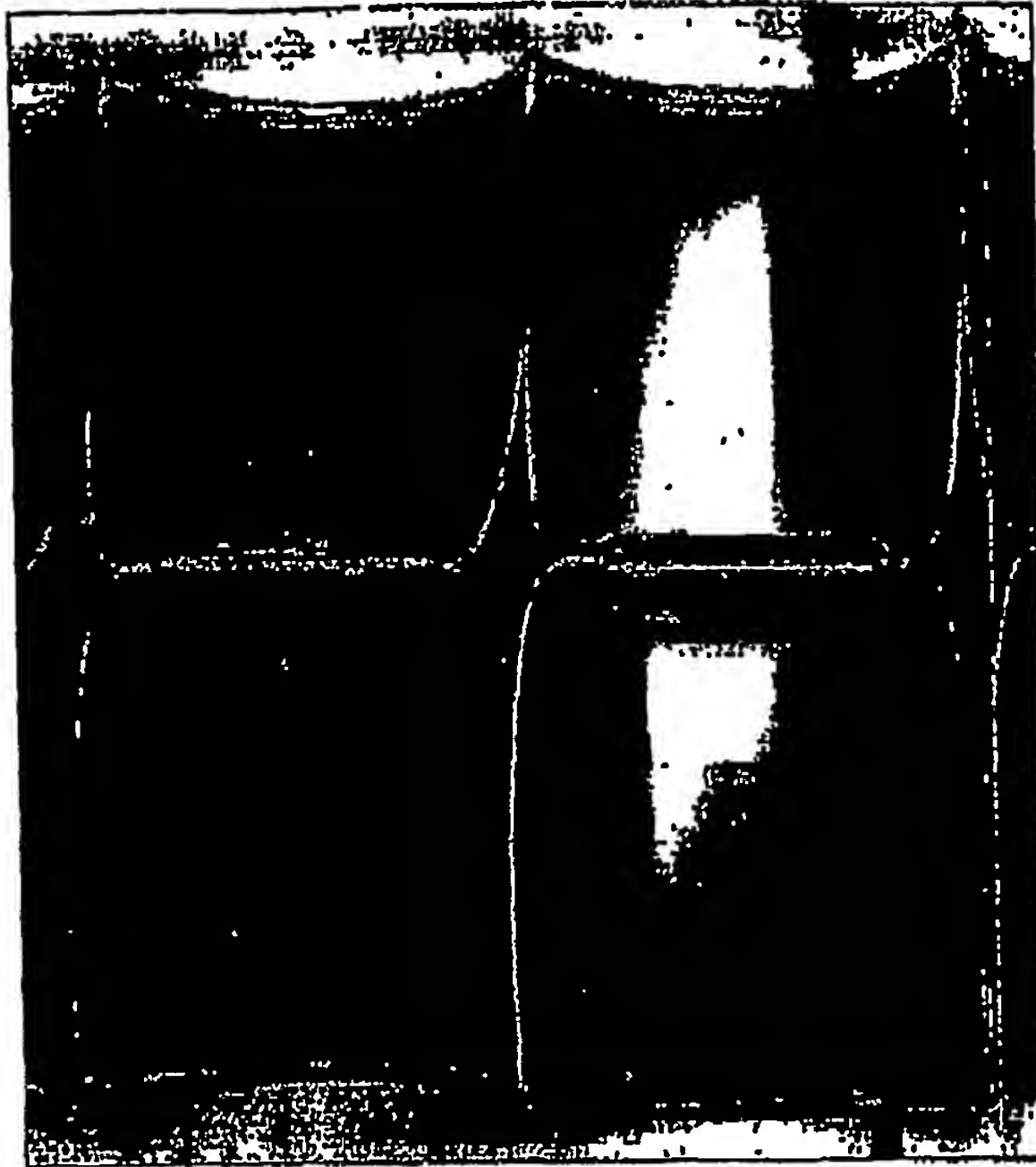


Fig. 1

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